A pH Electrode Switcher for Field Use with Slope and Standardization Controls

M. H. Holoka

Central and Arctic Region
Department of Fisheries and Oceans
Winnipeg, Manitoba R3T 2N6

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by

M. H. Holoka

Central and Arctic Region
Department of Fisheries and Oceans
Winnipeg, Manitoba R3T 2N6 CANADA

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TABLE OF CONTENTS

	Page
ABSTRACT/RÉSUMÉ	iv
INTRODUCTION	1
DESCRIPTION	1
CONSTRUCTION	2
RESULTS	3
DISCUSSION	3
REFERENCES	4

LIST OF TABLES

Table		Page
1	Comparison of apparatus and calibrator measurements	5
2	Switcher test readings	5
3	Parts list	6

LIST OF FIGURES

Figure		Page
1	Schematic diagram of switcher	7

ABSTRACT

HOLOKA, M.H. 1988. A pH electrode switcher for field use with slope and standardization controls. Can. Tech. Rep. Fish. Aquat. Sci. 1592: iv + 7 p.

This report describes the design, construction and operation of a field-oriented pH electrode switchbox, with slope and standardization controls. Flexibility in design allows the user to modify the unit to suit specific individual needs.

Keywords: pH electrode; switching.

RÉSUMÉ

HOLOKA, M.H. 1988. A pH electrode switcher for field use with slope and standardization controls. Can. Tech. Rep. Fish. Aquat. Sci. 1592: iv + 7 p.

Ce rapport décrit la conception, la fabrication et le fonctionnement d'un commutateur d'électrodes à pH, renforcé pour usage sur le terrain, doté de commandes de correction et d'étalonnage. L'appareil est conçu de telle façon que l'usager est en mesure de le modifier en fonction de ses besoins particuliers.

Mots-clés: électrode à pH; commutations.

INTRODUCTION

While conducting field research on acid precipitation, the need arose to sequentially and repeatedly measure the pH of water samples in several carboys in order to titrate them. To avoid cross contamination and minimize stabilization time, either a number of pH meters or a pH electrode switching device was required. Commercially available, battery-powered switchers were limited in number and utility. Their circuitry could only adjust the standardization potential which resulted in inaccurate readings when using different makes of electrodes. Even similar makes of electrodes of different age (efficiencies) caused difficulties. In order to alleviate this problem, a portable switchbox was designed with full standardization and slope (temperature) functions for each channel. The additional abuses given to a field instrument were taken into account.

DESCRIPTION

The electrode switcher was designed as a set of electronic building blocks each with its own specific function. While not as elegant as a completely integrated approach, it made construction and any trouble-shooting simple. Block A. (Fig. 1), consisting of integrated circuit IC1 and passive parts, is configured as a unity gain voltage follower. This stage, with its typical 10^{12} ohm input impedance, negligibly loads a pH electrode. It acts as a buffer between the high impedance potential produced by the electrode in its response to pH and the subsequent signal conditioning circuitry. The output of this stage is at the same voltage as the pH electrode but at a much lower impedance. This informational voltage can now be manipulated with much less likelihood of undesirable change.

Block B. (Fig. 1) consisting of integrated circuit IC2 and passive components is configured as an inverting amplifier with a variable gain. The reason for this amplifier stems from the term 2.3RT/nf in the Nernst equation which mathematically describes electrode behaviour, where R and F are constants. T is temperature (°K), and n is the charge on the ion, which is equal to 59.16 mV at 25°C. Thus, in the case of an 100% efficient pH electrode at 25°C, a change of 59.16 mV occurs for each 10-fold change in the activity of a monovalent ion, or per pH unit. Therefore, this voltage must be multiplied or amplified by a factor of approximately 1.7, so that on a digital display a reading in even pH units will result. The output of this stage changes 100 mV per pH unit when the slope is correctly calibrated. The potentiometer on IC2 which varies its gain is the unit's slope control.

Block C (Fig. 1) consists of a temperature compensated band gap reference and associated circuitry, forming an independent variable voltage source. Since the output of Block B registers 100 mV's per pH unit it will read 0 mV at pH 7, this being the isopotential point. Readings of +100 mV and -100 mV will be registered when measuring a pH of 6 and 8, respectively. In order to correctly display these voltages as pH, a voltage of 700 mV has to be algebraically added to the output of Block B. Block C performs this function. The potentiometer on the voltage reference can vary the correcting voltage from 600 to 800 mV ensuring adequate range. This potentiometer is the standardization control. The output of Block C can be read on any high

impedance digital volt meter or field pH meter on the millivolt scale directly as pH. Only the decimal point will be missing. Blocks A-C comprise one complete electrode channel. This circuit can be repeated as many times as necessary.

Block D (Fig. 1) consists of power switches and channel selection circuitry. It is here that the actual switching occurs. The voltage signal is at a sufficiently low impedance that extraordinary precautions are not necessary. Blocks A-C were put on a small circuit board and copied, in our case, three times. Each channel thus had independent control of slope and standardization so electrode matching was now unnecessary. However, when changing channels both signal wires were switched so as to avoid any possible interaction.

Rather than use a field pH meter in the millivolt mode, an optional digital voltmeter was incorporated into the switchbox. Block E (Fig. 1) in this apparatus consists of an Intersil ICL7136 analog digital converter evaluation kit. It is configured as a digital voltmeter reading 1999 mV full scale and the decimal point fixed between the second and third digits to read pH to the 0.01 unit level.

CONSTRUCTION

Block E or the analog digital converter was constructed according to instructions supplied with the evaluation kit. The band gap reference circuitconsisting of parts Z1 and R9 - R12 (Fig. 1) were tack soldered onto the circuit board. The converter was calibrated according to instructions and mounted in a metal enclosure. Blocks A, B, and C were mounted on a 6 x 7 cm circuit board with a suitably etched pattern. The metal enclosure used (25 x 18 x 10 cm, Hammond 1426-0) could accommodate up to six channels without overcrowding. Holes were drilled in the front of the box for slope and standardization controls, power switches, and channel selector. An important consideration in maintaining the high impedance of the circuit was not to solder the input pin and resistor (R1) (Fig. 1) to the circuit board. This resistor should be directly soldered to the input jack and then to pin number 3 of IC1. This practice helps prevent any problems of signal irregularities at high impedances. Additionally, static discharges should be prevented while soldering the unit to prevent damage in the delicate CMOS structures in the semiconductors. Switch number 2 controls both power for the integrated circuits and the voltage reference. This switch and counterpart in other channels is turned on only for the inputs that are in use. Switch number 1 controls which channel's output is read by the voltmeter as pH. The number of position required in the switch is determined by the total number of channels. Power for the voltmeter and each individual channel's reference is supplied by AA batteries in suitable holders. The digital voltmeter requires six batteries in series for 9V, and each reference requires two batteries for 3V. As shown in Fig. 1, only four wires interconnect the switch box and voltmeter. Two are for 9V power and two are for voltage measurement. The signal lines use BNC type jacks and plugs as well as shielded cable.

RESULTS

Electronic performance was evaluated using a Cole Parmer 5657-10 pH/mV calibrator rated at ±0.1% accuracy. This device, in addition to reference voltages, provided a very high impedance (1000M ohm output which simulated a pH electrode. This feature allowed more testing flexibility without using a large series of buffers. Temperature effects, buffer contamination, and other causes of deviations were eliminated by using this calibrator. Each channel was two-point calibrated at a pH of 4 and 7 as would have been done with an electrode and buffers. This chosen pH interval bracketed the actual range of interest in lake water measurements. Linearity was checked using the calibrator's direct output which was at a low impedance. The calibrator's output was then switched to high impedance mode (1000 M ohm) and linearity was again checked. The results in Table 1 show that, in the range of environmental interest, linearity will not be a factor.

To test the switchbox under actual experimental conditions. three different types of electrodes of different age were used. Connected to the switcher were an Orion #910200, an Orion Ross electrode, and a Fisher microprobe #13-639-92. A series of buffers at pH 200, 4.01, 6.00, 7.00, 8.00, and 9.00, were used to take test readings. Each channel was two point calibrated and the series of buffers measured without recalibration or alteration of any controls. The results are shown in Table 2. The similarity in pH measurements between all electrodes ensures that measurement consistency between samples will be maintained.

To check for temperature stability, the device was first calibrated and then cooled to 3°C. A range of pH readings were taken. Then the apparatus was heated to 45°C. and the pH measured again. No differences were seen at those temperature extremes. To check for short term drift the apparatus was left on for 6 hours while reading a simulated pH of 6. No drift was evident. Long-term stability was measured by turning on the machine every second day without recalibration for two weeks and taking simulated pH readings from the calibrator. No drift occurred over this time period.

DISCUSSION

This device was designed to alleviate several field-related problems. Difficulties associated with this type of work were taken into account. Field instruments are exposed to wide temperature fluctuations. An instrument may first be in the shade and then in the sun. The resulting large temperature change can cause voltage offsets in electronic amplifiers which in turn are algebraically added to the actual measurement voltage. This source of error must be minimized.

In Blocks A and B (Fig. 1), the integrated circuits chosen were Intersil ICL 7650 chopper stabilized operational amplifiers. The use of these components helped satisfy the previously mentioned criteria for field instruments. Since pH information is measured as a voltage, minimization of any offsets and drifts is essential. The chopper stabilization of this integrated circuit gives it a typical offset of only 1 uV over the device's rated temperature range. In addition, the temperature coefficient of offset voltage is

typically 0.01 uV per °C. Since the actual pH measurement is taking place at the mV level, at least three orders of magnitude higher, these two sources of error are minimized. Troublesome periodic trimming of offset as required by other operational amplifies is also eliminated. In the case of the Block A amplifier where input parameters are important, the typical input bias current of 1.5 pA and input resistance of 10^{12} ohms ensure acceptable loading effects on the electrode. Readability of the display is important. For example, in a rocking boat a digital display is preferred because the inertia of a needle in an analog display results in imprecise readings. In addition, the digital display is less fragile than an analog display with its jewelled meter movement. The stability of a field instrument is imperative. Frequent recalibration away from the laboratory is difficult and inconvenient. The Intersil ICL8069 reference in its highest grade which has a maximum temperature coefficient of 0.001%/°C was used to provide the offset voltage in Block C. This specification ensures temperature stability.

Similarly, an external ICL8069 band gap reference was used for the digital voltmeter.

Due to the high impedance nature of a pH electrode's output, the possibility of altering this potential is high. To help ameliorate this problem, the electrodes themselves were not switched. The switching action took place after the signal conditioning in Block D. The lower impedances found here helped prevent innaccurate readings.

It is felt that problems in design and operation of a field apparatus of this type have been addressed and rectified. The performance and low construction cost makes this electrode switcher practical for use in field situations where multiple simultaneous measurements are required.

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HANDBOOK of electrode technology. 1982. Orion Research Incorporated.

HOT ideas in CMOS. 1983. Intersil Inc.

Table 1. Comparison of apparatus and calibrator measurements.

pH setting of calibrator	apparatus reading at low impedance	apparatus reading at high impedance
0	0	-
2.00	2.00	2.01
4.00	4.00	4.00
6.00	6.00	6.00
7.00	7.00	7.00
8.00	8.00	8.00
10.00	10.00	10.02
12.00	12.00	-
14.00	14.00	-

Table 2. Switcher test readings.

Buffer	Electrodes		
pH	Orion #910200	Orion Ross	Fisher 13-639-92
2.00	1.94	2.06	1.96
4.01	4.01	4.01	4.01
6.00	5.99	6.00	6.00
7.00	7.00	7.00	7.00
8.00	7.96	7.92	7.95
9.00	8.96	8.97	9.00

Table 3. Parts list.

RESISTORS (all 1/4 W metal film: unless noted)

R1	22M	CARBON
R2	10K	
R3	15K	
R4	5K	10 TURN POTENTIOMETER
R5	3.6K	
R6	5.5K	
R7	1K	10 TURN POTENTIOMETER
R8	5.4K	
R9-R10	27K	
R11	20K	10 TURN TRIMMER
R12	150K	

CAPACITORS

C1-C4	0.1 uF 100V Mylar

SEMICONDUCTORS

IC1-IC2	INTERSIL ICL 7650
IC3	INTERSIL ICL 7136 evaluation kit
Z1-Z2	INTERSIL ICL 8069 voltage reference

SWITCHES

SW1 multi-pole multi-position rotary switch (see text)
SW2 multi-pole multi-position rotary switch (see text)

MISCELLANEOUS

- metal enclosures
- battery holders
- AA batteries
- circuit board standoffs
- input jacks
- connecting wire
- shielded cable

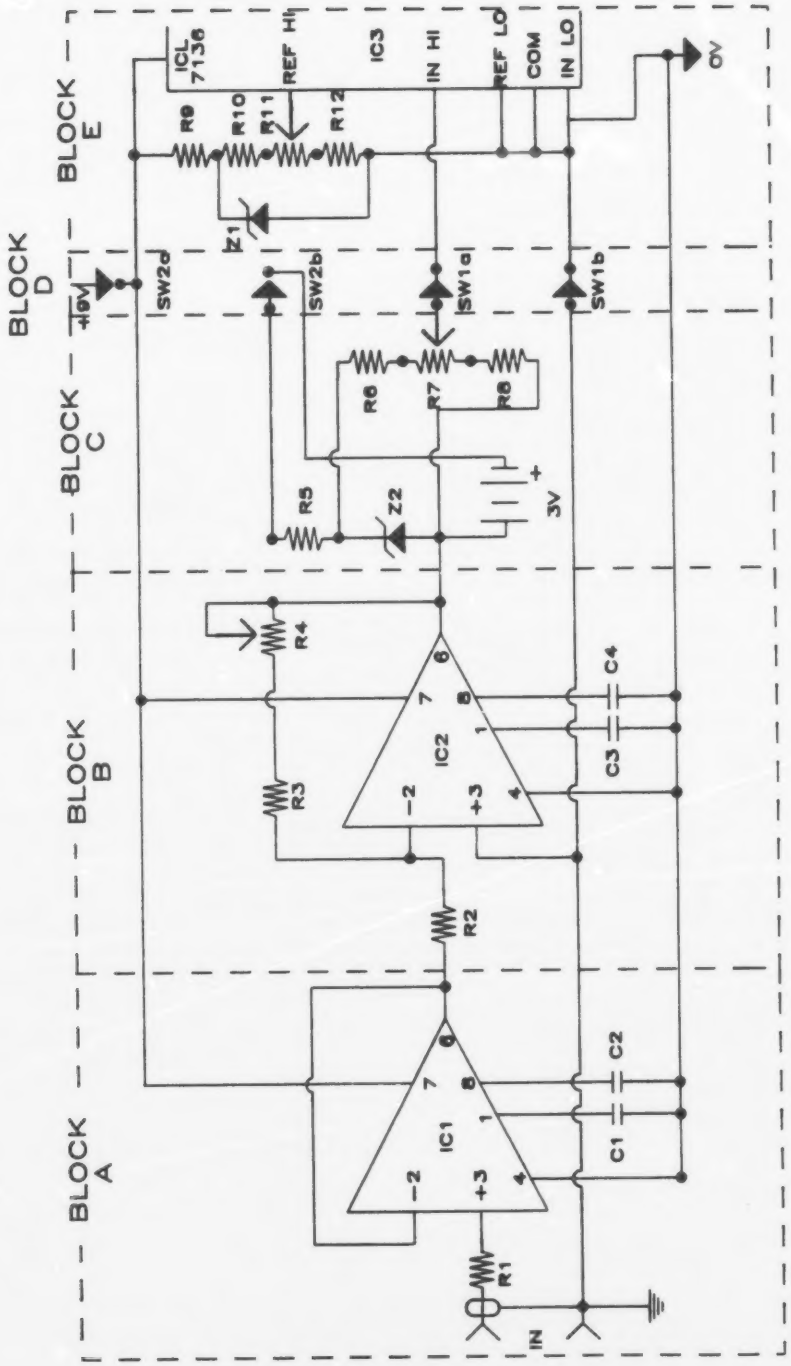

Fig. 1. Schematic diagram of switcher.